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10/01/01

December 21, 2001

**BOX PCT**

Commissioner for Patents  
Washington, D.C. 20231

PCT/FR00/01711  
-filed June 21, 2000

Re: Application of Jean-Pascal PLANCHE, Patrick TURELLO, Pierre CHAVEROT and  
Patrice VEGNY  
METHOD FOR THE PRODUCTION OF CROSS-LINKED AND/OR FUNCTIONALIZED  
BITUMEN/POLYMER COMPOSITIONS AND USE OF SAID COMPOSITIONS IN  
COVERINGS  
**Assignee: ELF ANTAR FRANCE**  
Our Ref: Q67797

Dear Sir:

The following documents and fees are submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty:

**The Declaration and Power of Attorney, English translation of the International Application and Assignment will be submitted at a later date.**

It is assumed that copies of the International Application, the International Search Report, the International Preliminary Examination Report, and any Articles 19 and 34 amendments as required by § 371(c) will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

The Government filing fee is calculated as follows:

Total claims	<u>22</u>	-	<u>20</u>	=	<u>2</u>	x	\$18.00	=	<u>\$36.00</u>
Independent claims	<u>1</u>	-	<u>3</u>	=	<u></u>	x	\$84.00	=	<u>\$0.00</u>
Base Fee									<u>\$890.00</u>
<b>TOTAL FEE</b>								<u>\$926.00</u>	

A check for the statutory filing fee of \$926.00 is attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from:

<u>Country</u>	<u>Application No</u>	<u>Filing Date</u>
France	99/07914	June 22, 1999

Respectfully submitted,

Mark Boland  
Registration No. 32,197

MXB/slb

1981876079003000

Rec'd PCT/PTG 01 OCT 2002

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Docket No: Q67797

Jean-Pascal PLANCHE, et al.

Appln. No.: 10/018,790

Group Art Unit: Unknown

Confirmation No.: 1942

Examiner: Unknown

Filed: December 21, 2001

For: METHOD FOR THE PRODUCTION OF CROSS-LINKED AND/OR  
FUNCTIONALIZED BITUMEN/POLYMER COMPOSITIONS AND USE OF  
SAID COMPOSITIONS IN COVERINGS (as amended)

**PRELIMINARY AMENDMENT**

**ATTN: BOX PCT**

Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination, please amend the above-identified application as follows:

**IN THE TITLE:**

**Please delete the present title and replace it with the following new**

**title:**

METHOD FOR THE PRODUCTION OF CROSS-LINKED AND/OR  
FUNCTIONALIZED BITUMEN/POLYMER COMPOSITIONS AND USE OF SAID  
COMPOSITIONS IN COVERINGS

**IN THE ABSTRACT:**

**Please insert the Abstract on the attached separate page.**

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**IN THE CLAIMS:**

**Please enter the following amended claims:**

1 (amended). A method for preparing cross-linked and/or functionalized bitumen/polymer compositions with a low susceptibility to temperature, wherein, when operating at temperatures that range between 100°C and 230°C and under agitation, forming a homogenous mass that represents the bitumen/polymer composition and is made of a bituminous matrix in which is uniformly dispersed a cross-linked and/or functionalized elastomer, made from a precursor elastomer used in a quantity that ranges between 0.5% and 30% of the weight of the bituminous matrix, where said method is characterized by making the bituminous matrix by associating, by weight, x% of a non oxidized bitumen with a penetrability that ranges between 20 and 900 and y% of an oxidized bitumen, with a penetrability that ranges between 10 and 90, where said penetrabilities are determined as set forth the in NF standard T 66004 and are expressed in 1/10 mm, where the values of x and y are such that  $20 \leq x \leq 95$  and  $5 \leq y \leq 80$  with  $x + y = 100$ .

2 (amended). The method as set forth in claim 1, characterized in that the weight percentages x% of non oxidized bitumen and y% of oxidized bitumen, associated to form the bituminous matrix of the bitumen/polymer composition are such that  $35 \leq x \leq 85$  and  $15 \leq y \leq 65$  with  $x + y = 100$ .

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3 (Amended). The method as set forth in claim 1, characterized in that the quantity of precursor elastomer represents from 1.5% to 20% of the weight of the bituminous matrix.

4 (Amended). The method as set forth in claim 1, characterized in that the non oxidized bitumen, entering in the making of the bituminous matrix, consists of one single bitumen or of a mixture of bitumens taken from among the straight-run bitumens, the refinery bitumens under reduced pressure, the propane or pentane deasphalting residues and viscosity breaking residues.

5 (amended). The method as set forth in claim 4, characterized in that the non oxidized bitumen is one bitumen or a mixture of bitumens taken from among the straight-run bitumens.

6 (Amended). The method as set forth in claim 1, characterized in that the oxidized bitumen, associated with the non oxidized bitumen to make up the bituminous matrix, consists of one single oxidized bitumen or of a mixture of oxidized bitumens taken from among the blown bitumens and the semi-blown bitumens.

7 (Amended). The method as set forth in claim 1, characterized in that the penetrability of the non oxidized bitumen, used in making the bituminous matrix, ranges between 35 and 500.

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8 (Amended). The method as set forth in claim 1, characterized in that the penetrability of the oxidized bitumen, used in making the bituminous matrix, ranges between 20 and 60.

9 (Amended). The method as set forth in claim 1, characterized in that the oxidized bitumen, associated with the non oxidized bitumen to make the bituminous matrix, has a ring and ball softening point as defined in the NF standard T 66008, that ranges between 60°C and 120°C.

10 (Amended). The method as set forth in claim 1, characterized in that the precursor elastomer consists of at least one copolymer chosen from among the random or block copolymers of styrene and of a conjugated diene, namely butadiene, isoprene, chloroprene, carboxylic butadiene or carboxylic isoprene.

11 (amended). The method as set forth in claim 10, characterized in that the precursor elastomer consists of one or several copolymers chosen from among the linear or star block copolymers, with or without a random hinge, of styrene and of butadiene, of styrene and of isoprene, of styrene and of chloroprene, of styrene and of carboxylic butadiene or alternatively of styrene and of carboxylic isoprene.

12 (Amended). The method as set forth in claim 10, characterized in that the copolymers of styrene and of conjugate diene have a styrene content that ranges between 5% and 50% by weight.

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13 (Amended). The method as set forth claim 10, characterized in that the copolymers of styrene and of conjugated diene have, prior to the cross-linking and/or functionalization, average molecular masses by weight that range between 10 000 daltons and 600 000 daltons.

14 (Amended). The method as set forth in claim 1, characterized in that it consists in putting the non oxidized bitumen and the oxidized bitumen chosen to make the bituminous matrix in contact with, by weight of said matrix, 0.5% to 30% of the precursor elastomer and 0.01% to 6% of cross-linking agent and/or a functionalization agent while working at temperatures that range between 100°C and 230°C and under agitation for a period of time of at least 5 minutes.

15 (Amended). The method as set forth in claim 14, characterized in that the precursor elastomer is put in contact with the non oxidized and the oxidized bitumens while working at temperatures ranging between 100°C and 230°C and under agitation for a period of time ranging from 5 minutes to 8 hours, to create a homogenous mixture, then the cross-linking agent and/or functionalization agent is incorporated into said mixture and it is all kept under agitation at temperatures ranging between 100C° and 230°C, and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized and the oxidized bitumens used to make the bituminous matrix, for a period of time that ranges

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between 5 minutes and 5 hours, to form a reaction product that makes up the cross-linked and/or functionalized bitumen/polymer composition.

16 (Amended). The method as set forth in claim 1, characterized in that it consists, in a first phase, in preparing a concentrate by putting from 50% to 100% of the non oxidized bitumen to be used to make the bituminous matrix in contact with, by weight of said matrix, 5% to 30% of the precursor elastomer and 0.01% to 6% of a cross-linking agent and/or a functionalization agent to form a cross-linked and/or functionalized bitumen/polymer reaction product that makes up said concentrate while working at temperatures ranging between 100°C and 230°C under agitation during a period of time of at least 5 minutes and then, in a second phase in diluting the cross-linked and/or functionalization bitumen/polymer reaction that resulted from the first phase and adding to it the oxidized bitumen and the possible remaining fraction of non oxidized bitumen, while operating at temperatures that range between 100°C and 230°C, under agitation, to form the cross-linked and/or functionalized bitumen/polymer composition.

17 (Amended). The method as set forth in claim 16, characterized in that the first phase is carried out by putting the precursor elastomer in contact with the non oxidized bitumen, while working at temperatures that range between 100°C and 230°C, and under agitation for a period of time from 5 minutes to 8 hours, to form a homogenous mass, then in adding to said mixture the cross-linking agent and/or

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functionalization agent and holding it all under agitation at temperatures that range between 100°C and 230°C, and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized bitumen, for a period of time that ranges from 5 minutes to 5 hours, to form the cross-linked and/or functionalized bitumen/polymer reaction product.

18 (Amended). The method as set forth in claim 14, characterized in that the functionalized elastomer is created within the bituminous matter using a functionalization agent selected from the group consisting of carboxylic acids or esters bearing thiol or disulfide groups and thiolcarboxylic acid polyesters.

19 (Amended). The method as set forth in claim 1, characterized in that the elastomer is functionalized and one or several reactive additives likely to react with the functional groupings of the elastomer are incorporated into the functionalized bitumen/polymer composition during its preparation where the quantity of the reactive additive(s) ranges from 0.01% to 10% of the weight of the bitumen present in the composition.

20 (Amended). The method as set forth in claim 14, characterized in that the cross-linked elastomer is created within the bituminous matrix, using a cross-linking agent selected from the group consisting of sulfur donor cross-linking agents and peroxidized compounds that generate free radicals at temperatures ranging between 100°C and 230°C.

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21 (Amended). The method as set forth in claim 1, further incorporating one or several additional polymers that are different from the precursor elastomer to the cross-linked and/or functionalized bitumen/polymer composition in an overall quantity that ranges between 0.3% and 20% of the weight of the bitumen of said compositions.

22 (Amended). A road surface pavement or a watertight facing made from a cross-linked and/or functionalized bitumen/polymer composition made from the method of claim 1.

**Please add the following new claims:**

23 (New). The method as set forth in claim 7, characterized in that the penetrability of the non oxidized bitumen, used in making the bituminous matrix, ranges between 160 and 330.

24 (New). The method as set forth in claim 13, characterized in that the copolymers of styrene and of conjugated diene have, prior to the cross-linking and/or functionalization, average molecular masses by weight that range 30 000 daltons and 400 000 daltons.

25 (New). The method as set forth in claim 14, characterized in that it consists in putting the non oxidized bitumen and the oxidized bitumen chosen to make the bituminous matrix in contact with, by weight of said matrix, 1.5% to 20% of the precursor elastomer and 0.05% to 3% of cross-linking agent and/or a

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functionalization agent while working at temperatures that range between 130°C and 200°C and under agitation for a period of time of at least 5 minutes.

26 (New). The method as set forth in claim 15, characterized in that the precursor elastomer is put in contact with the non oxidized and the oxidized bitumens while working at temperatures ranging between 130°C and 200°C and under agitation for a period of time ranging from 30 minutes to 6 hours, to create a homogenous mixture, then the cross-linking agent and/or functionalization agent is incorporated into said mixture and it is all kept under agitation at temperatures ranging between 130°C and 200°C, and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized and the oxidized bitumens used to make the bituminous matrix, for a period of time that ranges between 10 minutes and 180 minutes, to form a reaction product that makes up the cross-linked and/or functionalized bitumen/polymer composition.

27 (New). The method as set forth in claim 16, characterized in that it consists, in a first phase, in preparing a concentrate by putting from 50% to 100% of the non oxidized bitumen to be used to make the bituminous matrix in contact with, by weight of said matrix, 5% to 30% of the precursor elastomer and 0.05% to 3%, of a cross-linking agent and/or a functionalization agent to form a cross-linked and/or functionalized bitumen/polymer reaction product that makes up said concentrate while working at temperatures ranging between 130°C and 200°C, under agitation

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during a period of time of at least 5 minutes and then, in a second phase in diluting the cross-linked and/or functionalization bitumen/polymer reaction that resulted from the first phase and adding to it the oxidized bitumen and the possible remaining fraction of non oxidized bitumen, while operating at temperatures that range between 130°C and 200°C, under agitation, to form the cross-linked and/or functionalized bitumen/polymer composition.

28 (New). The method as set forth in claim 17, characterized in that the first phase is carried out by putting the precursor elastomer in contact with the non oxidized bitumen, while working at temperatures that range between 130°C and 200°C, and under agitation for a period of time from 30 minutes to 6 hours, to form a homogenous mass, then in adding to said mixture the cross-linking agent and/or functionalization agent and holding it all under agitation at temperatures that range between 130°C and 200°C and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized bitumen, for a period of time that ranges from between 10 minutes and 180 minutes, to form the cross-linked and/or functionalized bitumen/polymer reaction product.

29 (new). The method as set forth in claim 19, characterized in that the elastomer is functionalized and one or several reactive additives likely to react with the functional groupings of the elastomer are incorporated into the functionalized bitumen/polymer composition during its preparation where the quantity of the

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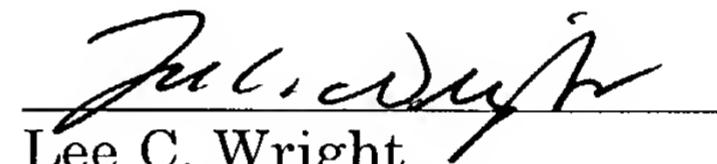
reactive additive(s) ranges from 0.05% to 5% of the weight of the bitumen present in the composition.

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**REMARKS**

The changes made to the claims are for clarity and to conform with U.S. claiming practice. New claims 23-29 correspond to the preferable subject matter of original claims 7, 13-17 and 19, respectively. Entry and consideration of this Amendment are respectfully requested.

Respectfully submitted,

  
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Date: October 1, 2002

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**APPENDIX**

**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE TITLE:**

The title is changed as follows:

METHOD FOR THE PRODUCTION OF [PREPARING] CROSS-LINKED  
AND/OR FUNCTIONALIZED BITUMEN/POLYMER COMPOSITIONS AND USE  
OF SAID COMPOSITIONS IN COVERINGS [THEIR APPLICATION IN THE  
MAKING OF PAVEMENTS]

**IN THE ABSTRACT:**

The following was inserted on a separate sheet as the abstract:

**ABSTRACT**

Compositions produced by forming a homogenous mass consisting of a  
bitumen matrix wherein a cross-linked and/or functionalized elastomer produced in  
situ from a precursor elastomer is dispersed in a uniform manner and makes up 0.5  
- 30% of the weight of the bitumen matrix. The bitumen matrix is created by  
associating 95 % - 20 wt. % non oxidized bitumen having a penetrability of 20-900  
and 5-80 wt. % oxidized bitumen having a penetrability of 10-90. The compositions  
can be used as bitumen binders in the production of coverings.

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**IN THE CLAIMS:**

**The claims are amended as follows:**

1 (amended). [– Method] A method for preparing cross-linked and/or functionalized bitumen/polymer compositions with a low susceptibility to temperature, wherein, when operating at temperatures that range between 100°C and 230°C and under agitation, [we form] forming a homogenous mass that represents the bitumen/polymer composition and is made of a bituminous matrix in which is uniformly dispersed a cross-linked and/or functionalized elastomer, made from a precursor elastomer used in a quantity that ranges between 0.5% and 30% of the weight of the bituminous matrix, where said method is characterized [in that we made] by making the bituminous matrix by associating, by weight, x% of a non oxidized bitumen with a penetrability that ranges between 20 and 900 and y% of an oxidized bitumen, with a penetrability that ranges between 10 and 90, where said penetrabilities are determined as set forth in the NF standard T 66004 and are expressed in 1/10 mm, where the values of x and y are such that  $20 \leq x \leq 95$  and  $5 \leq y \leq 80$  with  $x + y = 100$ .

2 (amended). The method [Method] as set forth in claim 1, characterized in that the weight percentages x% of non oxidized bitumen and y% of oxidized bitumen, associated to form the bituminous matrix of the bitumen/polymer composition are such that  $35 \leq x \leq 85$  and  $15 \leq y \leq 65$  with  $x + y = 100$ .

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3 (Amended). The method [Method] as set forth in claim 1 [or 2], characterized in that the quantity of precursor elastomer represents from 1.5% to 20% of the weight of the bituminous matrix.

4 (Amended). The method [Method] as set forth in [one of claims 1 through 3] claim 1, characterized in that the non oxidized bitumen, entering in the making of the bituminous matrix, consists of one single bitumen or of a mixture of bitumens taken from among the straight-run bitumens, the refinery bitumens under reduced pressure, the propane or pentane deasphalting residues and viscosity breaking residues.

5 (amended). The method [Method] as set forth in claim 4, characterized in that the non oxidized bitumen is one bitumen or a mixture of bitumens taken from among the straight-run bitumens.

6 (Amended). The method [Method] as set forth in [one of claims 1 through 5] claim 1, characterized in that the oxidized bitumen, associated with the non oxidized bitumen to make up the bituminous matrix, consists of one single oxidized bitumen or of a mixture of oxidized bitumens taken from among the blown bitumens and the semi-blown bitumens.

7 (Amended). The method [Method] as set forth in [one of claims 1 through 6] claim 1, characterized in that the penetrability of the non oxidized bitumen, used in

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making the bituminous matrix, ranges between 35 and 500 [and especially between 160 and 330].

8 (Amended). The method [Method] as set forth in [one of claims 1 through 7] claim 1, characterized in that the penetrability of the oxidized bitumen, used in making the bituminous matrix, ranges between 20 and 60.

9 (Amended). The method [Method] as set forth in [one of claims 1 through 8] claim 1, characterized in that the oxidized bitumen, associated with the non oxidized bitumen to make the bituminous matrix, has a ring and ball softening point as defined in the NF standard T 66008, that ranges between 60°C and 120°C.

10 (Amended). The method [Method] as set forth in [one of claims 1 through 9] claim 1, characterized in that the precursor elastomer consists of at least one copolymer chosen from among the random or block copolymers of styrene and of a conjugated diene, namely butadiene, isoprene, chloroprene, carboxylic butadiene or carboxylic isoprene.

11 (amended). The method [Method] as set forth in claim 10, characterized in that the precursor elastomer consists of one or several copolymers chosen from among the linear or star block copolymers, with or without a random hinge, of styrene and of butadiene, of styrene and of isoprene, of styrene and of chloroprene, of styrene and of carboxylic butadiene or alternatively of styrene and of carboxylic isoprene.

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12 (Amended). The method [Method] as set forth in claim 10 [or 11], characterized in that the copolymers of styrene and of conjugate diene have a styrene content that ranges between 5% and 50% by weight.

13 (Amended). The method [Method] as set forth [in one of claims 10 through 12] claim 10, characterized in that the copolymers of styrene and of conjugated diene have, prior to the cross-linking and/or functionalization, average molecular masses by weight that range between 10 000 daltons and 600 000 daltons [and preferably between 30 000 daltons and 400 000 daltons].

14 (Amended). The method [Method] as set forth in [one of claims 1 through 13] claim 1, characterized in that it consists in putting the non oxidized bitumen and the oxidized bitumen chosen to make the bituminous matrix in contact with, by weight of said matrix, 0.5% to 30% [and preferably 1.5% to 20%] of the precursor elastomer and 0.01% to 6% [and more particularly 0.05% to 3%,] of cross-linking agent and/or a functionalization agent while working at temperatures that range between 100°C and 230°C [and preferably between 130°C and 200°C] and under agitation for a period of time of at least 5 minutes.

15 (Amended). The method [Method] as set forth in claim 14, characterized in that the precursor elastomer is put in contact with the non oxidized and the oxidized bitumens while working at temperatures ranging between 100°C and 230°C[, preferably between 130°C and 200°C] and under agitation for a period of

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time ranging from 5 minutes to 8 hours, [in particular from 30 minutes to 6 hours,] to create a homogenous mixture, then the cross-linking agent and/or functionalization agent is incorporated into said mixture and it is all kept under agitation at temperatures ranging between 100°C and 230°C, [preferably between 130°C and 200°C,] and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized and the oxidized bitumens used to make the bituminous matrix, for a period of time that ranges between 5 minutes and 5 hours, [more particularly between 10 minutes and 180 minutes,] to form a reaction product that makes up the cross-linked and/or functionalized bitumen/polymer composition.

16 (Amended). The method [Method] as set forth in [one of claims 1 through 13] claim 1, characterized in that it consists, in a first phase, in preparing a concentrate by putting from 50% to 100% of the non oxidized bitumen to be used to make the bituminous matrix in contact with, by weight of said matrix, 5% to 30% of the precursor elastomer and 0.01% to 6%[, and more particularly 0.05% to 3%,] of a cross-linking agent and/or a functionalization agent to form a cross-linked and/or functionalized bitumen/polymer reaction product that makes up said concentrate while working at temperatures ranging between 100°C and 230°C[, and preferably between 130°C and 200°C,] under agitation during a period of time of at least 5 minutes and then [in], in a second phase in diluting the cross-linked and/or

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functionalization bitumen/polymer reaction that resulted from the first phase and adding to it the oxidized bitumen and the possible remaining fraction of non oxidized bitumen, while operating at temperatures that range between 100°C and 230°C, [preferably between 130°C and 200°C,] under agitation, to form the cross-linked and/or functionalized bitumen/polymer composition.

17 (Amended). The method [Method] as set forth in claim 16, characterized in that the first phase is carried out by putting the precursor elastomer in contact with the non oxidized bitumen, while working at temperatures that range between 100°C and 230°C, [preferably between 130°C and 200°C,] and under agitation for a period of time from 5 minutes to 8 hours, [namely from 30 minutes to 6 hours,] to form a homogenous mass, then in adding to said mixture the cross-linking agent and/or functionalization agent and holding it all under agitation at temperatures that range between 100°C and 230°C, [preferably between 130°C and 200°C] and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized bitumen, for a period of time that ranges from 5 minutes to 5 hours, [more particularly between 10 minutes and 180 minutes,] to form the cross-linked and/or functionalized bitumen/polymer reaction product.

18 (Amended). The method [Method] as set forth in [one of claims 14 through 17] claim 14, characterized in that the functionalized elastomer is created within the bituminous matter using a functionalization agent[, namely a functionalization

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agent taken from among the] selected from the group consisting of carboxylic acids or esters bearing thiol or disulfide [groupings] groups and [or from among the] thiolcarboxylic acid polyesters.

19 (Amended). The method [Method] as set forth in [one of claims 1 through 18] claim 1, characterized in that the elastomer is functionalized and [in that we incorporate] one or several reactive additives likely to react with the functional groupings of the elastomer are incorporated into the functionalized bitumen/polymer composition during its preparation where the quantity of the reactive additive(s) ranges from 0.01% to 10% [and more particularly from 0.05% to 5%] of the weight of the bitumen present in the composition.

20 (Amended). The method [Method] as set forth in [one of claims 14 through 17] claim 14, characterized in that the cross-linked elastomer is created within the bituminous matrix, using a cross-linking agent[, namely a cross-linking agent of the] selected from the group consisting of sulfur donor cross-linking [agent type of the] agents and peroxidized [compound type] compounds that generate[s] free radicals at temperatures ranging between 100°C and 230°C.

21 (Amended). The method [Method] as set forth in [one of claims 1 through 20] claim 1, [characterized in that we incorporate] further incorporating one or several additional polymers that are different from the precursor elastomer to the cross-linked and/or functionalized bitumen/polymer composition in an overall

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quantity that ranges between 0.3% and 20% [and preferably between 0.5% and 10%] of the weight of the bitumen of said compositions.

22 (Amended). [Application of the compositions obtained by the method as set forth in any one of claims 1 through 21, as bituminous binders that can be used immediately or following an aqueous emulsion, to make pavements and in particular] A road surface pavement[s, namely of the top coating type, for the making of coated materials that are spread when hot or cold,] or [alternatively for the making of] a watertight facing[s] made from a cross-linked and/or functionalized bitumen/polymer composition made from the method of claim 1.

**Claims 23-28 are added as new claims.**

## ABSTRACT

Compositions produced by forming a homogenous mass consisting of a bitumen matrix wherein a cross-linked and/or functionalized elastomer produced in situ from a precursor elastomer is dispersed in a uniform manner and makes up 0.5 - 30% of the weight of the bitumen matrix. The bitumen matrix is created by associating 95 % - 20 wt. % non oxidized bitumen having a penetrability of 20-900 and 5-80 wt. % oxidized bitumen having a penetrability of 10-90. The compositions can be used as bitumen binders in the production of coverings.

10/018790

Rec'd PENTYPO 01 OCT 2002

METHOD FOR PREPARING CROSS-LINKED AND/OR FUNCTIONALIZED BITUMEN/POLYMER COMPOSITIONS AND THEIR APPLICATION IN THE MAKING OF PAVEMENTS

The invention relates to a method for preparing cross-linked and/or functionalized bitumen/polymer compositions with a very low susceptibility to temperature. It also relates to the application of said compositions in the making of pavements and, in particular, road surface treatments, coated materials or watertight facings.

We know of the use of bituminous compositions as various top courses and in particular as roadway surface sealing coats provided said compositions have a certain number of essential mechanical characteristics.

These mechanical qualities are valued, in practice, by determining, through standardized tests, a series of mechanical properties, of which the most used are as follows:

- softening point, expressed in °C and determined by the Ring and Ball test defined by the NF standard T 66008,

- brittleness point, or Fraas point, expressed in °C and determined according to the IP standard 80/53,

- penetrability, expressed in 1/10 of a mm and determined according to the NF standard T 66004,

- tensile rheological characteristics determined according to the NF standard T 46002 and in the following quantities:

- yield stress  $\sigma_s$  in MPa,
- elongation at yield  $\epsilon_s$  in %,
- breaking stress  $\sigma_r$  in MPa,
- elongation at break  $\epsilon_r$  in %.

We can also obtain an indication of the susceptibility to temperature of bituminous compositions from a correlation between the penetrability (abbreviated pen) and the softening point (abbreviated RBT) of said compositions, known under the name PFEIFFER number (abbreviated PN).

This number is calculated using the formula:

20 - 500 A

**PN** = \_\_\_\_\_

1 + 50 A

where A is the slope of a straight line represented by the equation:

$$\log_{10}800 - \log_{10}\text{open}$$

$$A = \underline{\hspace{1cm}}$$

RBT - 25

The bituminous composition's susceptibility to temperature is all the more brittle as the value of the PFEIFFER number is large, or, as the value of the quantity A is smaller, which is the same thing. For refinery bitumens, the PFEIFFER number takes on negative values.

In general, traditional bitumens do not have all the required qualities at the same time and we have known for a long time that by adding various polymers to said traditional bitumens we are able to favorably modify the mechanical properties of the latter and create bitumen/polymer compositions with improved mechanical qualities compared to those of the bitumens alone.

The polymers that are likely to be added to the bitumens are most often elastomers such as polyisoprene, butyl rubber, polybutene, polyisobutene, ethylene vinyl acetate copolymers, polymethacrylates, polychloroprene, ethylene propylene copolymers, ethylene propylene diene terpolymers (EPDM), polynorbornene or alternatively random or block copolymers of styrene and of a conjugated diene.

Among the polymers added to the bitumens, the random or block copolymers of styrene and of conjugated diene and alternatively of styrene and of butadiene are particularly efficient as they dissolve easily in the bitumens and provide them with excellent mechanical and dynamic properties and namely very good viscoelasticity properties.

We also know that the stability of bitumen/polymer compositions in which the polymer added to the bitumen is an elastomer, namely a copolymer of styrene and of conjugated diene such as butadiene, can be improved by reactions, done in situ, of chemical coupling of the polymer with the bitumen, using a sulfur donor coupling agent (FR-A-2376188, FR-A-2429241, FR-A-2528439 and EP-A-360656), or of functionalization of the polymer using a functionalization agent of the acid or carboxylic

ester type with thiol or disulfide groups (WO-A-9714754 ) or of the thiolcarboxylic acid polyester type (WO-A-9847967).

We have now found that we can still improve some mechanical and rheological properties, namely consistency and tensile mechanical properties, and reduce the susceptibility to temperature of bitumen/polymer compositions, called cross-linked and/or functionalized bitumen/polymer compositions, obtained from the reaction of the chemical coupling of the polymer and the bitumen and/or of the functionalization of the polymer, when the bitumen used in the preparation of the cross-linked and/or functionalized bitumen/polymer composition contained an appropriate quantity of oxidized bitumen.

Therefore the invention relates to a method for preparing cross-linked and/or functionalized bitumen/polymer compositions with a very low susceptibility to temperature, wherein, when operating at temperatures that range between 100°C and 230°C, preferably between 130°C and 200°C, and when stirred, we form a homogenous mass that represents the bitumen/polymer composition and is made of a bituminous matrix wherein is evenly dispersed a cross-linked and/or functionalized elastomer, made from a precursor elastomer in a quantity ranging between 0.5% and 30% and more specifically between 1.5% and 20% of the weight of the bituminous matrix, where said method is characterized in that we make the bituminous matrix by associating, by weight, x% of a non oxidized bitumen, with a penetrability ranging between 20 and 900 and y% of an oxidized bitumen, with a penetrability that ranges between 10 and 90, where said penetrabilities are determined based on the NF standard T 66004 and expressed in 1/10 of a mm, where x and y are such that  $20 \leq x \leq 95$  and  $5 \leq y \leq 80$  with  $x + y = 100$ .

Advantageously, the percentages by weight x% of non oxidized bitumen and y% of oxidized bitumen, associated to form the bituminous matrix of the bitumen/polymer composition, are such that  $35 \leq x \leq 85$  and  $15 \leq y \leq 65$  with  $x + y = 100$ .

The non oxidized bitumen, used to form part of the bitumen matrix, consists of one single bitumen or a mixture of bitumens advantageously taken from among straight-run bitumen, refinery bitumens under reduced pressure, propane or pentane deasphalting residue and viscosity breaking residue. More specifically, the non oxidized bitumen is a bitumen or a mixture of bitumens taken from among straight-run bitumens.

The oxidized bitumen, used to form the other part of the bituminous matrix, consists of one single oxidized bitumen or of a mixture of oxidized bitumens advantageously chosen from among blown bitumens and semi-blown bitumens.

Advantageously, the penetrability of the non oxidized bitumen that is part of the bituminous matrix composition ranges between 35 and 500 and especially between 160 and 330. Whereas the penetrability of the oxidized bitumen, associated to the non oxidized bitumen to form said matrix, it ranges more specifically between 20 and 60.

According to a preferred method of execution, the oxidized bitumen used in making the bituminous matrix has a ring and ball softening point, defined as set forth in the NF standard T 66008, ranging between 60°C and 120°C.

The cross-linked and/or functionalized elastomer, present in the bitumen/polymer composition generated by the method as set forth in the invention, is created by cross-linking and/or functionalization of, a precursor elastomer such as polyisoprene, polynorbornene, polybutadiene, butyl rubber, ethylene propylene diene terpolymer (EPDM). Advantageously, the precursor elastomer consists of at least one copolymer chosen from among the random or block copolymers of styrene and of a conjugated diene such as butadiene, isoprene, chloroprene, carboxylic butadiene or carboxylic isoprene. More specifically, the precursor elastomer consists of one or several copolymers chosen from among the linear or star block copolymers, with or without a random hinge, of styrene and of butadiene, of styrene and of isoprene, of styrene and of chloroprene, of styrene and of carboxylic butadiene or alternatively of styrene and of carboxylic isoprene. The precursor copolymers of styrene and of conjugated diene, and in particular each of the afore-mentioned copolymers, advantageously have a styrene content that ranges between 5% and 50% by weight. These copolymers of styrene and of conjugated diene, and namely the above-mentioned copolymers, have, prior to cross-linking and/or functionalization, average molecular masses by weight that range, for example, between 10 000 daltons and 600 000 daltons and preferably between 30 000 daltons and 400 000 daltons. Preferably, the precursor copolymers of styrene and of conjugated diene are chosen from among the di or triblock copolymers of styrene and of butadiene, of styrene and of isoprene, of styrene and of carboxylic butadiene or alternatively of styrene and of

carboxylic isoprene, whose average molecular masses by weight and styrene weight content fall within the previously defined ranges.

The cross-linked and/or functionalized elastomer present in the bitumen/polymer composition prepared using the method as set forth in the invention, in particular one or the other of the cross-linked and/or functionalized elastomers generated by cross-linking and/or functionalization of the afore-mentioned precursor elastomers, can result, for example, from the sulfur cross-linking of the precursor elastomer and/or a functionalization of said precursor elastomer.

According to a first form of implementation, the method for preparing cross-linked and/or functionalized bitumen/polymer compositions consists in putting the non oxidized bitumen and the oxidized bitumen chosen to make the bituminous matrix in contact with, by weight of said matrix, 0.5% to 30% and preferably 1.5% to 20% of a precursor elastomer, namely a non cross-linked and non functionalized elastomer, and 0.01% and 6%, more particularly 0.05% to 3% of a cross-linking agent and/or a functionalization agent, while operating at temperatures ranging between 100°C and 230°C, preferably between 130°C and 200°C and while stirring for at least 5 minutes.

Preferably, in this first form of implementation, initially the precursor elastomer is put in contact with non oxidized and the oxidized bitumens while working at temperatures that range between 100°C and 230°C, preferably between 130°C and 200°C, and while stirring for a period of time ranging between 5 minutes and 8 hours, in particular between 30 minutes and 6 hours, to form a homogenous mixture, then the cross-linking agent and/or functionalization agent is added to said mixture in an appropriate quantity chosen within the previously defined ranges for said quantity, and it is all kept under agitation at temperatures ranging between 100°C and 230°C, preferably between 130°C and 200°C, that are identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized and oxidized bitumens that form the bituminous matrix, for a period ranging between 5 minutes and 5 hours, more particularly between 10 minutes and 180 minutes, to form a reaction product that constitutes the cross-linked and/or functionalized bitumen/polymer composition.

According to a second form of implementation, the method for preparing cross-linked and/or functionalized bitumen/polymer compositions consists, in a first phase, in

preparing a concentrate by putting between 50% and 100% of non oxidized bitumen making up the composition of the bituminous matrix, with, by weight of said matrix, 5% to 30% of the precursor elastomer and 0.01% to 6%, and more particularly 0.05% to 3%, of a cross-linking agent and/or a functionalization agent, while operating at temperatures ranging between 100°C and 230°C, preferably between 130°C and 200°C under agitation for at least 5 minutes, to form a cross-linked and/or functionalized bitumen/polymer reaction product, then, in a second phase, in diluting the cross-linked and/or functionalized bitumen/polymer reaction product that resulted from the first phase, by incorporating into it the oxidized bitumen and the possible remaining cut of non oxidized bitumen, while operating at temperatures ranging between 100°C and 230°C, preferably between 130°C and 200°C, and stirring, to form the cross-linked and/or functionalized bitumen/polymer composition.

Preferably, the first phase of this second form of implementation is implemented by first putting the precursor bitumen in contact with the non oxidized bitumen, while operating at temperatures ranging between 100°C and 230°C, preferably between 130°C and 200°C, and stirring for a period of time ranging between 5 minutes and 8 hours, in particular between 30 minutes and 6 hours, to form a homogenous mixture, then incorporating the cross-linking agent and/or functionalization agent into said mixture, in an appropriate quantity chosen from among the previously defined ranges for said quantity, and while still stirring it all and keeping it at temperatures ranging between 100°C and 230°C, preferably between 130°C and 200°C, and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized bitumen, for a period of time ranging between 5 minutes and 5 hours, more particularly between 10 minutes and 180 minutes, to form the cross-linked and/or functionalized bitumen/polymer reaction product.

The cross-linking agent used in the above-mentioned forms of implementation to form the cross-linked elastomer within the bituminous matrix from the precursor elastomer, may alternatively be a cross-linking agent of the sulfur donor type or a cross-linking agent of the peroxygen compound type that generates free radical at temperatures ranging between 100°C and 230°C.

The crosslinking sulfur donor agent may consist of a product chosen from the group that includes elementary sulfur, hydrocarbyl polysulfides, sulfur donor vulcanization accelerators, mixtures of said products together and/or with non sulfur donor vulcanization accelerators. In particular, the sulfur donor cross-linking agent can be chosen from among the M products that contain, by weight, from 0% to 100% of a CA component consisting of one or several sulfur donor vulcanization accelerators and from 100% to 0% of a CB component consisting of one or several vulcanization agents chosen from among elementary sulfur and hydrocarbyl polysulfides, and the N products, that contain a CC component consisting of one or several non sulfur donor vulcanization accelerators and an M product in a weight ratio of the CC component to the M product that ranges between 0.01 and 1 and preferably between 0.05 and 0.5.

The elemental sulfur likely to be used to make part or all the cross-linking agent is advantageously elemental sulfur and preferably crystallized sulfur in the orthorhombic form and known under the name of alpha sulfur.

The hydrocarbyl polysulfides likely to be used to form a part or all of the cross-linking agent can be chosen from among the various hydrocarbyl polysulfides defined in the French patent FR-A-2528439 and include, by preference, the polysulfides with a formula of  $R_{11} - (S)p - R_{11}$ , where  $R_{11}$  designates a tertiododecyl, hexadecyl, nonyl, decyl, and  $-(S)p-$  represents a divalent grouping formed by linking of p sulfur atoms where p is a whole number between 2 and 5.

When the cross-linking agent contains a sulfur donor vulcanization accelerator, the latter can be chosen, in particular, from among the thiuram polysulfides, alkylphenol disulfides and disulfides such as morpholine disulfide and caprolactam N,N'-disulfide, that are mentioned in the European patents EP-A-0360656 and EP-A-0409683.

Also, the non sulfur donor vulcanization accelerators that can be used to create the CC component of the cross-linking agents of the N product type can be sulfur compounds chosen from among compounds such as mercaptobenzothiazole and its derivatives, namely metallic thiolate benzothiazole and most of all the benzothiazolesulfenamides, metallic dithiocarbamates and thiuram monosulfides that are defined in the European patents EP-A-0360656 and EP-A-0409683.

Other non sulfur donor vulcanization accelerators, that do not belong to the families defined above, can also be used to create the CC component. Such vulcanization accelerators can be such as diphenyl-1,3 guanidine, diorthotolylguanidine and zinc oxide, where the latter compound may be used in the presence of fatty acid.

Due to its composition, as indicated above, the sulfur donor cross-linking agent can be of the single component type or the multiple component type, where the cross-linking agent of the multiple component type can be created prior to its use or alternatively produced *in situ* in the environment in which it must be present. The pre-created cross-linking agent of the multiple component type or of the single component type or the components of the multiple component type cross-linking agent created *in situ* can be used as they are, for example in a molten state, or in a mixture, for example in a solution or in suspension with a diluent, for example a hydrocarbon compound.

The peroxidized compound that generates free radicals at temperatures ranging between 100°C and 230°C, that can be used as a cross-linking agent to produce the cross-linked elastomer within the bituminous matrix, can be chosen, namely, from among the dihydrocarbyl peroxides such as, for example, ditertiobutyl peroxide and dicumyl peroxide.

The functionalization agent that is used to produce the functionalized elastomer, preferably within the bituminous matrix, through a reaction with the precursor elastomer, can consist of a product chosen from among carboxylic acids or esters with thiol or disulfide groupings, and in particular from among those of said carboxylic acids or esters that are suggested for this purpose in the WO-A-9714754 document, or from among the thiolcarboxylic acid polyesters, modified or not, and in particular from among those of said polyesters that are suggested for this purpose in the WO-A-9847967 document.

For further details on the implementation of cross-linking or functionalization agents, for the production of the cross-linked or functionalized elastomer within the bituminous matrix, we can refer in particular to the following documents, FR-A-2528439, EP-A-0360656 and EP-A-0409683 as far as the cross-linking agent is concerned, and to WO-A-9714754 and WO-A-9847967 as far as the functionalization agent is concerned, as the content of said documents is incorporated in this description by reference.

In addition to the cross-linked and/or functionalized elastomer, the cross-linked and/or functionalized bitumen/polymer composition as set forth in the invention can also contain one or several additional polymers different from said cross-linked and/or functionalized elastomer, where said additional polymer or polymers are in particular olefinic polymers such as polyethylene, polypropylene, polybutene, polyisobutene, vinyl ethylene/acetate copolymers, ethylene/propylene copolymers, ethylene/acrylate or alkyl methacrylate copolymers, functionalized olefinic polymers bearing epoxy or COOH groupings such as ethylene/acrylate or glycidyl methacrylate copolymers, ethylene/acrylate or alkyl/acrylate methacrylate or glycidyl methacrylate terpolymers and in particular glycidyl methyl/methacrylate ethylene/acrylate terpolymers and ethylene/acrylate or maleic alkyl/anhydride methacrylate terpolymers and in particular maleic butyl/anhydride ethylene/acrylate terpolymers.

The quantity of the additional polymer or polymers in the cross-linked and/or functionalized bitumen/polymer composition can range between 0.3% and 20% and preferably between 0.5% and 10% by overall weight of the bitumen in said composition.

The possible additional polymer(s) are advantageously incorporated in the bituminous matrix when the precursor elastomer is incorporated into said matrix, prior to the cross-linking or the functionalization.

During its making, between 1% and 40% and more particularly between 2% and 30% by weight of the bitumen of a fluxing agent can be added to the cross-linked and/or functionalized bitumen/polymer composition and can consist in particular of a hydrocarbon oil with a distillation range at atmospheric pressure that is determined in accordance with the ASTM standard D 86-67, ranging between 100°C and 600°C and ranging more specifically between 150°C and 350°C. This hydrocarbon oil, which can among others be a petroleum fraction of aromatic nature, a naphtheno-paraffin-base petroleum fraction, a paraffin-based petroleum fraction, a coal oil or an oil of plant origin, is sufficiently “heavy” to limit the evaporation when it is added to the bitumen and also sufficiently “light” to be eliminated as much as possible after spreading the bitumen/polymer composition in which it is contained, so as to once again find the same mechanical properties that the bitumen/polymer composition prepared without the use of a fluxing agent has after being spread when hot. The fluxing agent can be added to the

environment that is created from the bitumen, the precursor elastomer and, if necessary, the possible additional polymer(s) and the cross-linking agent and/or the functionalization agent, at any time during the making of said environment, with the quantity of fluxing agent being chosen, within the ranges defined above, to be compatible with the final sought use at the work site.

During its formation, the reaction product that makes up the functionalized bitumen/polymer composition, can advantageously be added, while operating at temperatures ranging between 100°C and 230°C and more specifically between 130°C and 200°C, with one or several additives likely to react with the functional groups, for example the carboxylic acids or esters carried by the functionalized elastomer and possibly by the bitumen of the functionalized bitumen/polymer composition, to activate or strengthen the link between the macromolecular links of said functionalized elastomer and/or between said macromolecular links and the bitumen and thus strengthen the physicomechanical properties of the functionalized bitumen/polymer composition. In particular, these reactive additives can be amines, namely primary or secondary polyamines, alcohols, namely polyols, aminoalcohols, epoxides, acids, namely polyacids, or alternatively metallic compounds. Examples of such appropriate additives are given, in particular, in documents WO-A-9714754 and WO-A-9847967.

The quantity of the afore-mentioned reactive additive or additives, that is incorporated into the reaction environment to give birth to the functionalized bitumen/polymer compositions, can go from 0.01% to 10% and more particularly from 0.05% to 5% by weight of bitumen present in said reaction environment.

We can also incorporate additives conventionally used in cross-linked and/or functionalized bitumen/polymer compositions such as promoters of adhesion of the cross-linked and/or functionalized bitumen/polymer composition to mineral surfaces of loads such as French chalk, carbon black, used tires reduced to powder, to the environment that produces the cross-linked and/or functionalized bitumen/polymer compositions at any time during the making of said environment.

In one form of implementation of the production of the cross-linked and/or functionalized bitumen/polymer composition that uses a hydrocarbon oil such as defined above, as a fluxing agent, the precursor elastomer, the possible additional polymer(s) and,

if so desired, the cross-linking agent and/or the functionalization agent are incorporated in the bitumen in the form of a mother solution of these products in the hydrocarbon oil that makes up the fluxing agent.

The mother solution is prepared by putting the ingredients of which it is made in contact with each other, namely hydrocarbon oil serving as a solvent, precursor elastomer, and if present, additional polymer(s) and cross-linking agent and/or functionalized agent, under agitation, at temperatures that range between 10°C and 170°C and more specifically between 40°C and 120°C, for a sufficient period of time, for example ranging between 10 minutes and 2 hours, to obtain a full dissolution of the polymeric ingredients and the cross-linking agent and/or the functionalization agent in the hydrocarbon oil.

The respective concentrations of the precursor elastomer and, if present, the additional polymer(s) and the cross-linking agent and/or the functionalization agent, in the mother solution, can vary quite largely based, in particular, on the nature of the hydrocarbon oil used to dissolve said polymer ingredients and the cross-linking agent and/or functionalization agent. Advantageously, the mother solution contains a quantity of precursor elastomer that represents between 5% and 40% and more specifically between 10% and 30% of the weight of the hydrocarbon oil. When present in the mother solution, the cross-linking agent and/or functionalization agent, is used in a quantity ranging, in particular, between 0.05% and 15% and more particularly between 0.1% and 8% of the weight of the hydrocarbon oil.

To prepare the cross-linked and/or functionalized bitumen/polymer compositions or the cross-linked and/or functionalized bitumen/polymer concentrates using the mother solution technique, we mix the mother solution that contains the precursor elastomer and, if used, the additional polymers and the cross-linking agent and/or functionalization agent with the bitumen at temperatures ranging between 100°C and 230°C, more specifically between 130°C and 200°C while stirring, this being done, for example, by incorporating the mother solution to the bitumen still being stirred, at temperatures between 100°C and 230°C and more specifically between 130°C and 200°C, then we keep stirring the mixture resulting therefrom and keep it at temperatures ranging between 100°C and 230°C and more specifically between 130°C and 200°C, for example at the temperatures

used to make the mixture of the mother solution and the bitumen , for at least 5 minutes, and generally between 10 minutes and 2 hours, to create a product that makes the cross-linked and/or functionalized bitumen/polymer composition or the cross-linked and/or functionalized bitumen/polymer concentrate.

The quantity of mother solution mixed with the bitumen is chosen to provide the desired quantities, in relation to the bitumen, of precursor elastomer, additional polymer(s) and cross-linking agent and/or functionalization agent, where said quantities fall in the ranges as previously defined.

Immediately after obtaining it, the cross-linked and/or functionalized bitumen/polymer composition, produced by the method as set forth in the invention, can be subjected to a treatment using an acid adjuvant, for example made of at least one acid chosen from among phosphoric acid, sulfuric acid, polyphosphoric acids, sulfonic acids, and phosphonic acids, as described in the documents WO-A-9528446 and WO-A-9714753.

The cross-linked and/or functionalized bitumen/polymer compositions produced as set forth in the invention can be used as bituminous binders, either directly or after an aqueous emulsion, to make pavements and in particular road surface treatments, namely of the sealing coat type, for the making of coated materials that are spread when hot or cold, or alternatively to make watertight facings.

The invention is illustrated in the following examples given for informational purposes only and not to be considered limiting.

In these examples, the quantities and percentages are expressed by weight unless otherwise noted.

Furthermore, the rheological and mechanical properties of the bitumens or the bitumen/polymer compositions to which we refer in said examples, namely penetrability, ring and ball softening point and PFEIFFER number (PN), are those that have been previously defined.

#### EXAMPLES 1 THROUGH 9

We prepared control cross-linked bitumen/polymer compositions (examples 1 through 3), as well as cross-linked bitumen/polymer compositions as set forth in the

invention (examples 4 through 7) to evaluate and compare the physicomechanical properties.

We worked under the following conditions:

Example 1 (control)

In a reactor held at 180°C and under agitation, we introduced 964 parts of a straight-run bitumen with a penetrability, determined based on the provisions of the NF standard T 66004, equal to 55 and 35 parts of diblock of styrene and of butadiene with a molecular mass by weight equal to 125 000 Daltons and containing, by weight, 25% of styrene and 75% of butadiene. The content of the reactor was then kept at 180°C under agitation for a period of time equal to 2 hours to form a homogenous mass. We then added 1 part of sulfur as a cross-linking agent to said mass and kept the reaction environment so created at 180°C, under agitation, for 2 hours to produce a control cross-linked bitumen/polymer composition.

Example 2 (control):

We prepared a cross-linked bitumen/polymer composition working as described in example 1, using however 948 parts of bitumen, 50 parts of the diblock copolymer of styrene and of butadiene and 2 parts of sulfur.

Example 3 (control):

We prepared a cross-linked bitumen/polymer concentrate working as follows:

In a reactor held at 180°C and under agitation, we incorporated 15 parts of a resin acid that contained 50% of active matter, to 863 parts of a straight-run bitumen whose penetrability was determined as set forth in the provisions of the NF standard T 66004, equal to 190 and kept the mixture so obtained at said temperature for 20 minutes.

Still working at a temperature of 180°C, we then incorporated, under agitation, 120 parts of a diblock copolymer of styrene and of butadiene identical to that used in example 1 to the bitumen and resin acid mix. The content of the reactor was then kept at 180°C under agitation for a period of time equal to 2 hours to produce a homogenous mass. To said mass we then added 2 parts of sulfur, as a cross-linking agent, and kept the reaction environment thus created at 180°C, under agitation, for 2 hours to produce a control cross-linked bitumen/polymer concentrate. Said concentrate had a penetrability of 96, a ring and ball softening point of 84°C and a Pfeiffer number of 6.85.

We then diluted said concentrate with a straight-run bitumen with a penetrability of 27 and a ring and ball softening point (RBT) of 58.5°C, while mixing for 20 minutes, at 180°C and under agitation, 30 parts of the concentrate and 70 parts of the straight-run bitumen, to obtain a diluted cross-linked bitumen/polymer composition that contained 3.6% of cross-linked block copolymer.

Example 4 (as set forth in the invention):

We prepared a cross-linked bitumen/polymer composition working as described in example 1, replacing however the bitumen used with a mixture of 420 parts of a straight-run bitumen, with a penetrability ranging between 180 and 220, and 544 parts of an oxidized bitumen of the semi-blown type, with a penetrability ranging between 20 and 30, and a ring and ball softening point (RBT) ranging between 75 and 85°C.

Example 5 (as set forth in the invention):

We prepared a cross-linked bitumen/polymer composition working as described in example 1, replacing however the bitumens used with a mixture of 617 parts of a straight-run bitumen, with a penetrability ranging between 180 and 220, and 347 parts of an oxidized bitumen of the semi-blown type, with a penetrability of 40 and a ring and ball softening point (RBT) of 100°C.

Example 6 (as set forth in the invention):

We prepared a cross-linked bitumen/polymer composition, playing the role of a concentrate, working as described in example 1, replacing however the bitumen with 923 parts of straight-run bitumen with a penetrability ranging between 180 and 220 and using 75 parts of the diblock copolymer of styrene and of butadiene and 2 parts of sulfur.

We then diluted the concentrate obtained with an oxidized bitumen of the semi-blown type with a penetrability ranging between 20 and 30 and a ring and ball softening point (RBT) ranging between 75 and 85°C. To do so, we mixed said concentrate for 20 minutes, at 180°C and under agitation, with 952 parts of oxidized bitumen, to obtain a diluted cross-linked bitumen/polymer composition that contained 4% of cross-linked block copolymer.

Example 7 (as set forth in the invention):

We prepared a cross-linked bitumen/polymer concentrate, working as described in example 3. Said concentrate had a penetrability of 96, a ring and ball softening point (RBT) of 84°C and a Pfeiffer number of 6.85.

We then diluted the concentrate obtained with a mixture of bitumens made of 75% of a straight-run bitumen, with a penetrability of 27 and a ring and ball softening point (RBT) of 58.5°C and 25% of an oxidized bitumen of the semi-blown type with a penetrability of 40 and a ring and ball softening point (RBT) of 101°C. The dilution was done by mixing 30 parts of said concentrate with 70 parts of the bitumen mixture for 20 minutes, at 180°C under agitation; the diluted cross-linked bitumen/polymer composition obtained contained 3.7% of cross-linked block copolymer.

For each of the compositions prepared as indicated in examples 1 through 7, we determined the following properties:

- penetrability at 25°C (Pen)
- ring and ball softening point (RBT)
- PFEIFFER number (PN)

The results obtained are provided in the following table.

The polymer content of the compositions is expressed in weight percentages of the overall amount of bitumen.

Table

Examples							
Copolymer in the final composition (% of overall bitumen)	3.6	5.3	3.75	3.6	3.6	4	3.75
Oxidized bitumen in the final composition (% of overall bitumen)	0	0	0	56.5	36	50.8	18.4
Pen (1/10 mm)	46	46	35	45	30	58	48
RBT (°C)	61	68	60.5	69.2	80	69.4	63
PN	1.0	2.3	0.29	2.4	3.1	3.1	1.5

In view of the properties in the above table, it seems that:

- replacement of a part of the non oxidized bitumen with oxidized bitumen in the cross-linked bitumen/polymer composition is translated by an improvement of the physical properties of said compositions and in particular by an increase of the ring and ball softening point (RBT) and of the Pfeiffer number, whether the oxidized bitumen is present during the preparation of the cross-linked bitumen/polymer compositions (compare the results in the control example 1 with those of examples 4 and 5 as set forth in the invention) or whether it is only used during the dilution of the cross-linked bitumen/polymer concentrates (compare the results of the control example 3 with those of example 7 as set forth in the invention), to produce the cross-linked bitumen/polymer compositions;
- replacement of a part of the non oxidized bitumen with oxidized bitumen in the cross-linked bitumen/polymer compositions makes it possible, with comparable properties of penetrability, ring and ball softening point (RBT) and Pfeiffer number, to reduce the composition's content of cross-linked polymer (compare the results of the control example 2 with those of the example 4 as set forth in the invention).

CLAIMS

1 – Method for preparing cross-linked and/or functionalized bitumen/polymer compositions with a low susceptibility to temperature, wherein, when operating at temperatures that range between 100°C and 230°C and under agitation, we form a homogenous mass that represents the bitumen/polymer composition and is made of a bituminous matrix in which is uniformly dispersed a cross-linked and/or functionalized elastomer, made from a precursor elastomer used in a quantity that ranges between 0.5% and 30% of the weight of the bituminous matrix, where said method is characterized in that we made the bituminous matrix by associating, by weight, x% of a non oxidized bitumen with a penetrability that ranges between 20 and 900 and y% of an oxidized bitumen, with a penetrability that ranges between 10 and 90, where said penetrabilities are determined as set forth the NF standard T 66004 and are expressed in 1/10 mm, where the values of x and y are such that  $20 \leq x \leq 95$  and  $5 \leq y \leq 80$  with  $x + y = 100$ .

2. Method as set forth in claim 1, characterized in that the weight percentages x% of non oxidized bitumen and y% of oxidized bitumen, associated to form the bituminous matrix of the bitumen/polymer composition are such that  $35 \leq x \leq 85$  and  $15 \leq y \leq 65$  with  $x + y = 100$ .

3. Method as set forth in claim 1 or 2, characterized in that the quantity of precursor elastomer represents from 1.5% to 20% of the weight of the bituminous matrix.

4. Method as set forth in one of claims 1 through 3, characterized in that the non oxidized bitumen, entering in the making of the bituminous matrix, consist of one single bitumen or of a mixture of bitumens taken from among the straight-run bitumens, the refinery bitumens under reduced pressure, the propane or pentane deasphalting residues and viscosity breaking residues.

5. Method as set forth in claim 4, characterized in that the non oxidized bitumen is one bitumen or a mixture of bitumens taken from among the straight-run bitumens.

6. Method as set forth in one of claims 1 through 5, characterized in that the oxidized bitumen, associated with the non oxidized bitumen to make up the bituminous matrix, consists of one single oxidized bitumen or of a mixture of oxidized bitumens taken from among the blown bitumens and the semi-blown bitumens.

7. Method as set forth in one of claims 1 through 6, characterized in that the penetrability of the non oxidized bitumen, used in making the bituminous matrix, ranges between 35 and 500 and especially between 160 and 330.

8. Method as set forth in one of claims 1 through 7, characterized in that the penetrability of the oxidized bitumen, used in making the bituminous matrix ranges between 20 and 60.

9. Method as set forth in one of claims 1 through 8, characterized in that the oxidized bitumen, associated with the non oxidized bitumen to make the bituminous matrix has a ring and ball softening point as defined in the NF standard T 66008, that ranges between 60°C and 120°C.

10. Method as set forth in one of claims 1 through 9, characterized in that the precursor elastomer consists of at least one copolymer chosen from among the random or block copolymers of styrene and of a conjugated diene, namely butadiene, isoprene, chloroprene, carboxylic butadiene or carboxylic isoprene.

11. Method as set forth in claim 10, characterized in that the precursor elastomer consists of one or several copolymers chosen from among the linear or star block copolymers, with or without a random hinge, of styrene and of butadiene, of styrene and of isoprene, of styrene and of chloroprene, of styrene and of carboxylic butadiene or alternatively of styrene and of carboxylic isoprene.

12. Method as set forth in claim 10 or 11, characterized in that the copolymers of styrene and of conjugate diene have a styrene content that ranges between 5% and 50% by weight.

13. Method as set forth in one of claims 10 through 12, characterized in that the copolymers of styrene and of conjugated diene have, prior to the cross-linking and/or functionalization, average molecular masses by weight that range between 10 000 daltons and 600 000 daltons and preferably between 30 000 daltons and 400 000 daltons.

14. Method as set forth in one of claims 1 through 13, characterized in that it consists in putting the non oxidized bitumen and the oxidized bitumen chosen to make the bituminous matrix in contact with, by weight of said matrix, 0.5% to 30% and preferably 1.5% to 20% of the precursor elastomer and 0.01% to 6% and more particularly 0.05% to 3%, of cross-linking agent and/or a functionalization agent while

working at temperatures that range between 100°C and 230°C and preferably between 130°C and 200°C and under agitation for a period of time of at least 5 minutes.

15. Method as set forth in claim 14, characterized in that the precursor elastomer is put in contact with the non oxidized and the oxidized bitumens while working at temperatures ranging between 100°C and 230°C, preferably between 130°C and 200°C and under agitation for a period of time ranging from 5 minutes to 8 hours, in particular from 30 minutes to 6 hours, to create a homogenous mixture, then the cross-linking agent and/or functionalization agent is incorporated into said mixture and it is all kept under agitation at temperatures ranging between 100°C and 230°C, preferably between 130°C and 200°C, and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized and the oxidized bitumens used to make the bituminous matrix, for a period of time that ranges between 5 minutes and 5 hours, more particularly between 10 minutes and 180 minutes, to form a reaction product that makes up the cross-linked and/or functionalized bitumen/polymer composition.

16. Method as set forth in one of claims 1 through 13, characterized in that it consists, in a first phase, in preparing a concentrate by putting from 50% to 100% of the non oxidized bitumen to be used to make the bituminous matrix in contact with, by weight of said matrix, 5% to 30% of the precursor elastomer and 0.01% to 6%, and more particularly 0.05% to 3%, of a cross-linking agent and/or a functionalization agent to form a cross-linked and/or functionalized bitumen/polymer reaction product that makes up said concentrate while working at temperatures ranging between 100°C and 230°C, and preferably between 130°C and 200°C, under agitation during a period of time of at least 5 minutes and then in, in a second phase in diluting the cross-linked and/or functionalization bitumen/polymer reaction that resulted from the first phase and adding to it the oxidized bitumen and the possible remaining fraction of non oxidized bitumen, while operating at temperatures that range between 100°C and 230°C, preferably between 130°C and 200°C, under agitation, to form the cross-linked and/or functionalized bitumen/polymer composition.

17. Method as set forth in claim 16, characterized in that the first phase is carried out by putting the precursor elastomer in contact with the non oxidized bitumen, while working at temperatures that range between 100°C and 230°C, preferably between

130°C and 200°C, and under agitation for a period of time from 5 minutes to 8 hours, namely from 30 minutes to 6 hours, to form a homogenous mass, then in adding to said mixture the cross-linking agent and/or functionalization agent and holding it all under agitation at temperatures that range between 100°C and 230°C, preferably between 130°C and 200°C and identical or not to the temperatures at which the precursor elastomer is mixed with the non oxidized bitumen, for a period of time that ranges from 5 minutes to 5 hours, more particularly between 10 minutes and 180 minutes, to form the cross-linked and/or functionalized bitumen/polymer reaction product.

18. Method as set forth in one of claims 14 through 17, characterized in that the functionalized elastomer is created within the bituminous matter using a functionalization agent, namely a functionalization agent taken from among the carboxylic acids or esters bearing thiol or disulfide groupings or from among the thiocarboxylic acid polyesters.

19. Method as set forth in one of claims 1 through 18, characterized in that the elastomer is functionalized and in that we incorporate one or several reactive additives likely to react with the functional groupings of the elastomer into the functionalized bitumen/polymer composition during its preparation where the quantity of the reactive additive(s) ranges from 0.01% to 10% and more particularly from 0.05% to 5% of the weight of the bitumen present in the composition.

20. Method as set forth in one of claims 14 through 17, characterized in that the cross-linked elastomer is created within the bituminous matrix, using a cross-linking agent, namely a cross-linking agent of the sulfur donor cross-linking agent type of the peroxidized compound type that generates free radicals at temperatures ranging between 100°C and 230°C.

21. Method as set forth in one of claims 1 through 20, characterized in that we incorporate one or several additional polymers that are different from the precursor elastomer to the cross-linked and/or functionalized bitumen/polymer composition in an overall quantity that ranges between 0.3% and 20% and preferably between 0.5% and 10% of the weight of the bitumen of said compositions.

22. Application of the compositions obtained by the method as set forth in any one of claims 1 through 21, as bituminous binders that can be used immediately or following an aqueous emulsion, to make pavements and in particular road surface

pavements, namely of the top coating type, for the making of coated materials that are spread when hot or cold, or alternatively for the making of watertight facings.

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(54) Title: METHOD FOR THE PRODUCTION OF CROSS-LINKED AND/OR FUNCTIONALIZED BITUMEN/POLYMER COMPOSITIONS AND USE OF SAID COMPOSITIONS IN COVERINGS

(54) Titre: PROCEDE DE PREPARATION DE COMPOSITIONS BITUME/POLYMER RETICULEES ET/OU FONCTIONNALISEES ET LEUR APPLICATION A LA REALISATION DE REVETEMENTS

**A1**  
**WO 00/78870**

(57) Abstract: The invention relates to compositions which are produced by forming a homogeneous mass consisting of a bitumen matrix wherein a cross-linked and/or functionalized elastomer produced in situ from a precursor elastomer is dispersed in a uniform manner and makes up 0.5 - 30 % of the weight of the bitumen matrix. The bitumen matrix is created by associating 95 % -20 wt. % non oxidized bitumen having a penetrability of 200-900 and 5-80 wt. % oxidized bitumen having a penetrability of 10-90. Said compositions can be used as bitumen binders in the production of coverings.

(57) Abrégé: On prépare ces compositions en formant une masse homogène constituée d'une matrice bitumineuse dans laquelle est dispersé uniformément un élastomère réticulé et/ou fonctionnalisé produit in situ à partir d'un élastomère précurseur, qui est utilisé en quantité comprise entre 0,5 % et 30 % du poids de la matrice bitumineuse. On constitue la matrice bitumineuse en associant, en poids, de 95 % à 20 % de bitume non oxydé, ayant une pénétrabilité comprise entre 20 et 900, et de 5 % à 80 % de bitume oxydé, ayant une pénétrabilité comprise entre 10 et 90. Lesdites compositions sont utilisables comme liants bitumineux pour la réalisation de revêtements.

# Declaration and Power of Attorney for Patent Application

## Déclaration et pouvoirs pour demande de brevet

### French Language Declaration

En tant que l'inventeur nommé ci-après, je déclare par le présent acte que :

Mon domicile, mon adresse postale et ma nationalité sont ceux figurant ci-dessous à côté de mon nom.

Je crois être le premier inventeur original et unique (si un seul nom est mentionné ci-dessous), ou l'un des premiers co-inventeurs originaux (si plusieurs noms sont mentionnés ci-dessous) de l'objet revendiqué, pour lequel une demande de brevet a été déposée concernant l'invention intitulée

As a below named inventor, I hereby declare that:

My residence, mailing address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

### METHOD FOR THE PRODUCTION OF CROSS-LINKED AND/OR FUNCTIONALIZED BITUMEN/POLYMER COMPOSITIONS AND USE OF SAID COMPOSITIONS IN COVERINGS

et dont la description est fournie ci-joint à moins que la case suivante n'ait été cochée :

a été déposée le \_\_\_\_\_  
sous le numéro de demande des Etats-Unis ou le numéro  
de demande international PCT  
\_\_\_\_\_  
(n° de confirmation \_\_\_\_\_)  
et modifiée le \_\_\_\_\_  
(le cas échéant).

Je déclare par le présent acte avoir passé en revue et compris le contenu de la description ci-dessus, revendications comprises, telles que modifiées par toute modification dont il aura été fait référence ci-dessus.

Je reconnaiss devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations.

the specification of which is attached hereto unless the following box is checked:

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and was amended on  
\_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

## **French Language Declaration**

Je revendique par le présent acte avoir la priorité étrangère, en vertu du Titre 35, § 119(a)-(d) ou § 365(b) du Code des Etats-Unis, sur toute demande étrangère de brevet ou certificat d'inventeur ou, en vertu du Titre 35, § 365(a) du même Code, sur toute demande internationale PCT désignant au moins un pays autre que les Etats-Unis et figurant ci-dessous et, en cochant la case, j'ai aussi indiqué ci-dessous toute demande étrangère de brevet, tout certificat d'inventeur ou toute demande internationale PCT ayant une date de dépôt précédant celle de la demande à propos de laquelle une priorité est revendiquée.

Prior foreign application(s)  
Demande(s) de brevet antérieure(s)

99/07914      France  
(Number)      (Country)  
(Numéro)      (Pays)

(Number) (Numéro)	(Country) (Pays)
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Je revendique par le présent acte tout bénéfice, en vertu du Titre 35, § 120 du Code des Etats-Unis, de toute demande de brevet effectuée aux Etats-Unis, ou en vertu du Titre 35, § 365(c) du même Code, de toute demande internationale PCT désignant les Etats-Unis et figurant ci-dessous et, dans la mesure où l'objet de chacune des revendications de cette demande de brevet n'est pas divulgué dans la demande antérieure américaine ou internationale PCT, en vertu des dispositions du premier paragraphe du Titre 35, § 112 du Code des Etats-Unis, je reconnais devoir divulguer toute information pertinente à la brevetabilité, comme défini dans le Titre 37, § 1.56 du Code fédéral des réglementations, dont j'ai pu disposer entre la date de dépôt de la demande antérieure et la date de dépôt de la demande nationale ou internationale PCT de la présente demande :

(Application No.) (Filing Date)  
(N° de demande) (Date de dépôt)

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Je déclare par le présent acte que toute déclaration ci-incluse est, à ma connaissance, véridique et que toute déclaration formulée à partir de renseignements ou de suppositions est tenue pour véridique; et de plus, que toutes ces déclarations ont été formulées en sachant que toute fausse déclaration volontaire ou son équivalent est passible d'une amende ou d'une incarcération, ou des deux, en vertu de la Section 1001 du Titre 18 du Code des Etats-Unis, et que de telles déclarations volontairement fausses risquent de compromettre la validité de la demande de brevet ou du brevet délivré à partir de celle-ci.

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below, and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Claimed  
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I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Status: patented, pending, abandoned)  
(Statut : breveté, en cours d'examen, abandonné)

(Status: patented, pending, abandoned)  
(Statut : breveté, en cours d'examen, abandonné)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

## French Language Declaration

POUVOIRS : je désigne par les présentes tous avocats de SUGHRUE MION, PLLC énumérés sous le Numéro de Client USPTO figurant ci-après comme mes avocats pour poursuivre la présente procédure et traiter avec l'Office des brevets et des marques (*Patent and Trademark Office*) toute affaire en liaison avec celle-ci, reconnaissant formellement que les avocats spécifiques énumérés sous ce Numéro de Client peuvent être modifiés à tout moment, à la discréction exclusive de Sughrue Mion, PLLC, et demande que toute correspondance relative à la demande soit adressée à l'adresse mentionnée sous le même Numéro USPTO.

POWER OF ATTORNEY: I hereby appoint all attorneys of SUGHRUE MION, PLLC who are listed under the USPTO Customer Number shown below as my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith, recognizing that the specific attorneys listed under that Customer Number may be changed from time to time at the sole discretion of Sughrue Mion, PLLC, and request that all correspondence about the application be addressed to the address filed under the same USPTO Customer Number.



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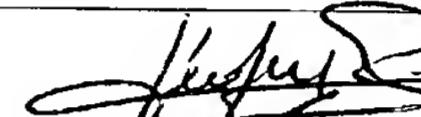
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Signature du cinquième inventeur	Date	Fifth inventor's signature Date
Domicile	Residence	
Nationalité	Citizenship	
Adresse postale	Mailing Address	
<b>Nom complet du sixième co-inventeur, le cas échéant</b>		<b>Full name of sixth joint inventor, if any</b>
Signature du sixième inventeur	Date	Sixth inventor's signature Date
Domicile	Residence	
Nationalité	Citizenship	
Adresse postale	Mailing Address	